

Electron Paramagnetic Resonance Study of Pr⁴⁺ Ions Doped in BaSnO₃, Ba₂SnO₄, and Ba₃Sn₂O₇

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The isotropic electron paramagnetic resonance (EPR) spectra of powders with Pr⁴⁺ doped in the cubic perovskite BaSnO₃ and the layered perovskites Ba₂SnO₄ and Ba₃Sn₂O₇ were measured at 4.2 K. Very large hyperfine interactions with the ¹⁴¹Pr nucleus were observed in all of the host materials. The results were analyzed based on the weak-field approximation, and the *g* values and hyperfine coupling constants *A* were obtained. The measured *g* values are much smaller than $|-10/7|$, showing that the crystal field effect on the behavior of a 4*f* electron is large. The value of $|g|$ decreases from 0.646 (Pr⁴⁺/Ba₂SnO₄) to 0.606 (Pr⁴⁺/Ba₃Sn₂O₇) to 0.583 (Pr⁴⁺/BaSnO₃), which is caused by the increase of the crystal field due to the shortening of the Pr⁴⁺–O²⁻ distance. On the other hand, the hyperfine coupling constants are almost constant: *A* = 0.060 cm⁻¹. © 1998 Academic Press

INTRODUCTION

The electronic configuration of the tetravalent praseodymium ion is [Xe]4*f*¹ ([Xe]: xenon electronic core). For electronic structure analysis, this *f*¹ configuration is straightforward, as only the crystal field and spin–orbit coupling interaction are important. When this ion is located in an octahedral crystal field environment, such a compound is especially suitable for studying the behavior of 4*f* electrons in solids, because it is easy to compare the experimental results with theoretical calculations.

Although the trivalent oxidation state is the most stable oxidation state of praseodymium, the tetravalent state is accessible. Perovskite-type oxides ABO₃, where *A* is a divalent ion (e.g., Sr or Ba), accommodate tetravalent metal ions at the *B* site of the crystal (1). The *B*-site ions sit at the center of the octahedron formed by six oxygen ions. Since tetravalent lanthanide and actinide ions can be incorporated into the *B* sites, this lattice type is useful for studying the magnetic properties of these ions in octahedral symmetry.

In an earlier study (2), we successfully measured for the first time the EPR spectrum of the Pr⁴⁺ ion in an octahedral crystal field by doping it in the perovskite BaCeO₃ (where

the Pr⁴⁺ ion is substituted for the Ce⁴⁺ ion) and lowering the experimental temperature to liquid helium temperature. In the EPR spectrum, a very large hyperfine interaction with the ¹⁴¹Pr nucleus (nuclear spin $I = \frac{5}{2}$) was measured. From the analysis of the spectrum, it was found that the crystal field influences the magnetic properties of a 4*f* electron.

Figure 1 shows the crystal structures of BaSnO₃, Ba₂SnO₄, and Ba₃Sn₂O₇. BaSnO₃ (Fig. 1a) has a cubic perovskite structure in which Sn⁴⁺ ions sit at the center of an octahedron formed by six oxygen ions. The basic structure components of the perovskites consist of three-dimensional frames of corner-shared SnO₆⁸⁻. Both Ba₂SnO₄ (Fig. 1b) and Ba₃Sn₂O₇ (Fig. 1c) are well-known Ruddlesden–Popper-type phases, which are expressed by the formula Ba_{*n*+1}Sn_{*n*}O_{3*n*+1} [$=n(\text{BaSnO}_3) \cdot \text{BaO}$, $n = 1, 2$]. In these phases, the three-dimensional frames are broken, and they involve a second kind of stacking unit of the perovskite layer: this results in a long-range-ordered two-dimensional structure.

To obtain further information on the behavior of 4*f* electrons in solids, we have paid attention to the sites of Sn⁴⁺ ions in the series of compounds shown in Fig. 1 and have prepared samples in which Pr⁴⁺ ions are doped in these compounds (the Pr⁴⁺ ions are substituted for the Sn⁴⁺ ions). Through analysis of their EPR spectra, the effect of the crystal field on the behavior of the 4*f* electron of the Pr⁴⁺ ion will be discussed.

EXPERIMENTAL

1. Sample Preparation

BaCO₃ (or SrCO₃), Pr₆O₁₁, and SnO₂ were used as starting materials. Before use, both Pr₆O₁₁ and SnO₂ were heated in air at 850°C to remove any moisture and to oxidize them to the stoichiometric compositions. They were weighed in the correct metal ratios (the concentration of the praseodymium ion (= Pr/(Pr + Sn)) is 0.01, 0.02, and 0.05), intimately mixed, and heated in a flowing oxygen atmosphere at 1300°C in an SiC resistance furnace for 1 day. After cooling to room temperature, the samples were

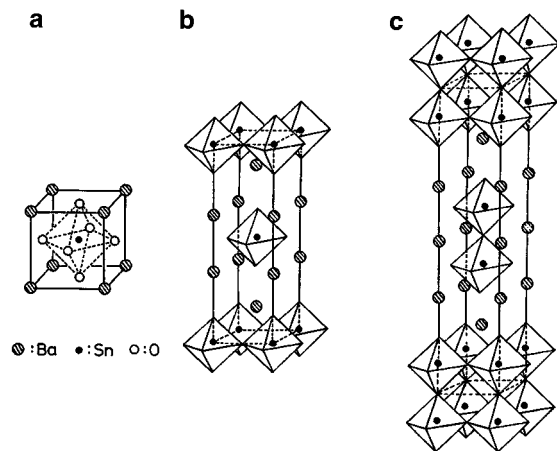


FIG. 1. Crystal structures of BaSnO₃ (a), Ba₂SnO₄ (b), and Ba₃Sn₂O₇ (c).

crushed into a powder, reground, re-pressed into pellets, and heated again under the same conditions to make the reaction complete.

2. Analysis

X-ray diffraction analysis was performed with CuK α radiation on a RINT 2000 diffractometer equipped with a curved graphite monochromator. The samples prepared in this study were formed in single phases.

3. Electron Paramagnetic Resonance Measurement

EPR spectra at X band (9.053 GHz) were measured using a JEOL RE-2X spectrometer operating with an Air Products Helitran cooling system. The magnetic field was swept from 100 to 13,500 G, which was monitored with a proton NMR gaussmeter, and the microwave frequency was measured with a frequency counter. Before the samples were measured, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or the sample tube.

RESULTS AND DISCUSSION

The EPR spectra could be measured at 4.2 K in any of the host materials. With increasing temperature, all the assigned absorption EPR lines become considerably weaker in intensity. This observation of the EPR spectra strongly indicates that the oxidation state of the praseodymium ion is not trivalent, but tetravalent, because the non-Kramers' Pr³⁺ ion usually shows no EPR spectrum (3).

Figure 2 shows the isotropic EPR spectrum for Pr⁴⁺ doped in BaSnO₃ measured at 4.2 K. Five absorption lines were observed. They are due to the hyperfine interaction

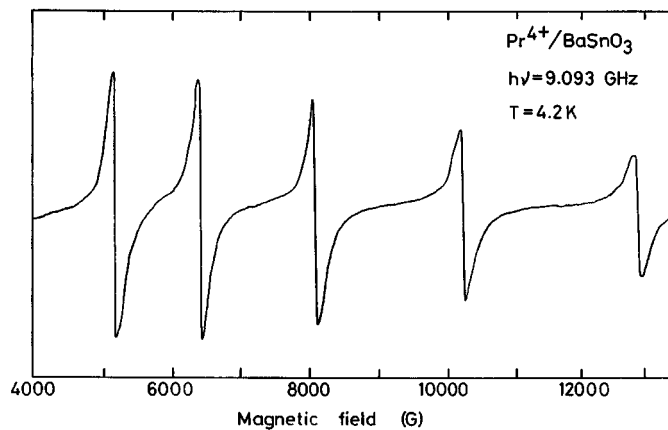


FIG. 2. EPR spectrum for Pr⁴⁺ ion doped in BaSnO₃ measured at 4.2 K.

with the nuclear spin for ¹⁴¹Pr ($I = \frac{5}{2}$) (natural abundance 100%). The isotropic spectrum for Pr⁴⁺ doped in BaSnO₃ indicates that the crystal field distortion from an octahedral field symmetry around the Pr⁴⁺ is negligible; i.e., the Pr⁴⁺ ion is substituted for the Sn⁴⁺ site. Since the nuclear spin for ¹⁴¹Pr is $\frac{5}{2}$, the number of EPR absorption lines due to the hyperfine interaction with the nuclear spin for ¹⁴¹Pr should be six. However, the number of measured absorption lines is not six, but five; i.e., the sixth absorption line due to the hyperfine interaction with the nuclear spin for ¹⁴¹Pr was not observed in this experiment.

The Spin Hamiltonian for the isotropic EPR spectrum of Pr⁴⁺ is

$$\mathcal{H} = g\beta H \cdot S' + AS' \cdot I - g'_N \beta H \cdot I \quad [1]$$

where g is the g value for Pr⁴⁺ with an effective spin $S' = \frac{1}{2}$, A is the hyperfine coupling constant, g'_N is the effective nuclear g value (in units of Bohr magnetons), β is the Bohr magneton, and H is the applied magnetic field. Usually the assumption can be made that the electronic Zeeman term (the first term on the right-hand side of Eq. [1]) is much larger than the hyperfine term (the second term on the right-hand side), which would result in a six-line spectrum for an isotropic resonance with $I = \frac{5}{2}$. In the Pr⁴⁺/BaSnO₃ spectrum, the spacings between the EPR absorption lines are large enough and they become wider with resonance magnetic field (see Fig. 2), which indicates that the electron spin quantum number (m_S) and the nuclear spin quantum number (m_I) are not good (pure) quantum numbers. We have to solve the Hamiltonian [1] exactly. The solution has been given by Ramsey (4) and others (5).

First, I and S are coupled together to form the resultant F , where $F = I + S$. For $S = \frac{1}{2}$ and $I = \frac{5}{2}$ in the absence of a magnetic field, there are two states $F = 2$ and $F = 3$ which

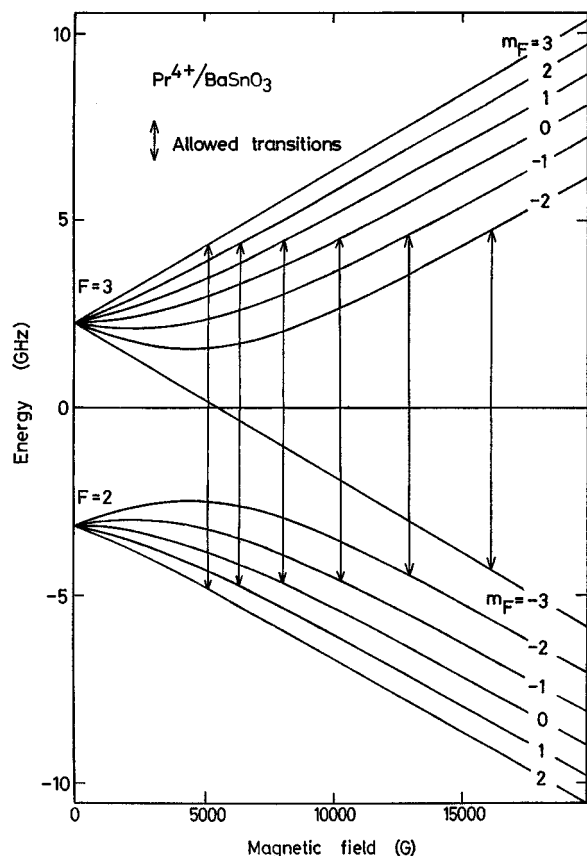


FIG. 3. Zeeman energy levels for Pr⁴⁺ in BaSnO₃. Arrows show the observable EPR transitions at 4.2 K.

are separated by $3A$. When the magnetic field is included, each of these two states splits into $(2F + 1) |m_F\rangle$ Zeeman levels, and six allowed transitions ($\Delta F = \pm 1$; $\Delta m_F = \pm 1$) are observable (see Fig. 3). When the observed EPR spectra are fit to the parameters of the spin-Hamiltonian [1], the best fit parameters are $|g| = 0.583$ and $A = 0.0589 \text{ cm}^{-1}$ for Pr⁴⁺/BaSnO₃ with g_N set equal to 0.0. The resonance field for the sixth allowed transition (the highest resonance field) is 16,078 G, which is beyond our maximum obtainable magnetic field (13,500 G). Figure 3 shows the Zeeman energy levels calculated for Pr⁴⁺ in BaSnO₃. Arrows show the observable EPR transitions.

Although the sign of the g value is not obtained by this experiment, comparison with other f^1 systems in octahedral symmetry, such as NpF₆/UF₆ (6) and Pa⁴⁺/Cs₂ZrCl₆ (5), where the sign of the g value has been measured, indicates that the g value for Pr⁴⁺/BaSnO₃ should be negative.

For a single f electron in an octahedral field, the sevenfold orbitally degenerate energy state is split into a singlet state Γ_2 and two triplet states Γ_4 and Γ_5 (see Fig. 4) (7). The energy difference between Γ_2 and Γ_5 is labeled Δ , and the energy difference between Γ_4 and Γ_5 is labeled Θ . When spin-orbit coupling is taken into account (with ζ the

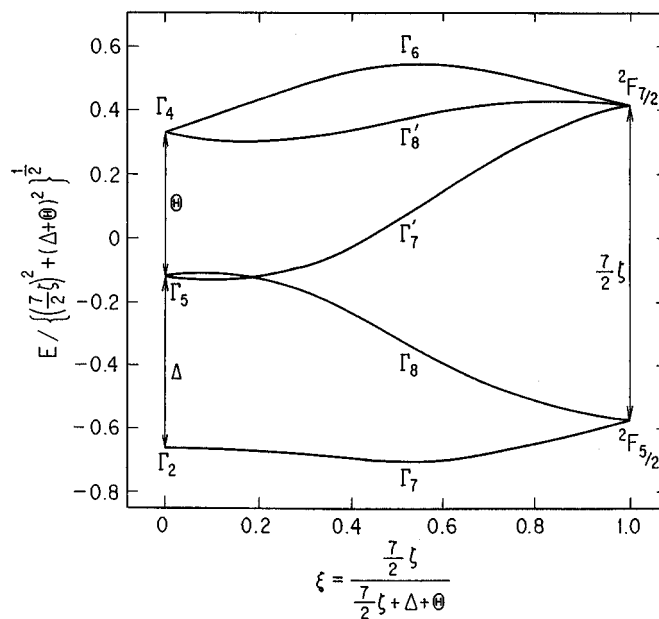


FIG. 4. Relative energy splittings of an f electron as the relative magnitudes of the crystal field (with octahedral symmetry) and spin-orbit coupling interactions change.

spin-orbit coupling constant), the Γ_2 orbital state is transformed into a doublet Γ_7 , and the Γ_5 and Γ_4 states are split into Γ_7' and Γ_8 , and Γ_6 and Γ_8' , respectively. The ground state Kramers' doublet is a Γ_7 state and is coupled to the excited Γ_7' state, arising from the Γ_5 orbital state, by the spin-orbit coupling.

The g value for the ground state Γ_7 doublet is calculated to be

$$g = 2\langle \Gamma_7 | L + 2S | \Gamma_7 \rangle \\ = 2\cos^2\theta - 4/\sqrt{3}\sin 2\theta, \quad [2]$$

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state, determined by the relation

$$\tan 2\theta = 2\sqrt{3}/(\Delta - \frac{1}{2}\zeta). \quad [3]$$

Equation [2] indicates that the g value for an f electron perturbed by an octahedral crystal field should be between $-10/7$ (for the Γ_7 ground doublet in the ${}^2F_{5/2}$ multiplet) and 2.00 (no spin-orbit interaction), and it increases from $-10/7$ with increasing crystal field strength (8,9).

The variation of the g value for an f^1 configuration in octahedral symmetry against $\Delta/(\frac{7}{2}\zeta)$ (ratio of the crystal field splitting to spin-orbit interaction) is shown in Fig. 5. In this figure, the g value for Pr⁴⁺/BaSnO₃ is plotted along with those for Pr⁴⁺/Ba₂SnO₄ and Pr⁴⁺/Ba₃Sn₂O₇ (which will be described later) and for Pa⁴⁺/Cs₂ZrCl₆ ($g = -1.142$,

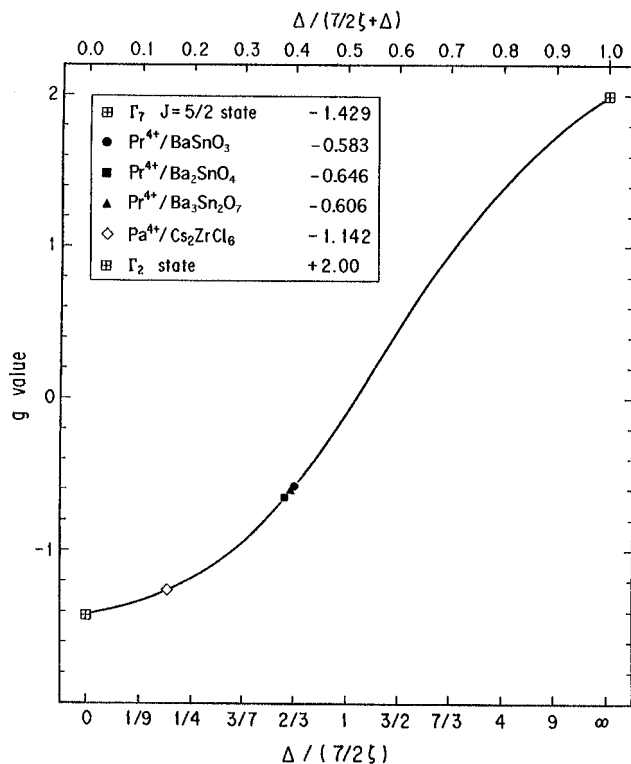


FIG. 5. g values vs the ratio $\Delta/(7/2\xi)$ for the f^1 configuration in octahedral symmetry.

weak crystal field) (5). The g value determined here for $\text{Pr}^{4+}/\text{BaSnO}_3$ is comparable to that for NpF_6/UF_6 ($g = -0.608$, strong crystal field) (6), which shows that the crystal field strength in $\text{Pr}^{4+}/\text{BaSnO}_3$ is as large as that in NpF_6/UF_6 .

Figure 6 shows the EPR spectrum for Pr^{4+} doped in Ba_2SnO_4 measured at 4.2 K. In the spectrum, several very weak absorption lines are observed along with its main EPR absorption lines. The positions and magnitudes at their very weak EPR absorption lines vary with Pr concentration (y value) in $\text{Ba}_2\text{Pr}_y\text{Sn}_{1-y}\text{O}_4$; they are considered to be attributable to other phases of the $\text{PrO}_2\text{-Ba}_2\text{SnO}_4$ system. When the observed EPR spectra are fit to the parameters of the spin-Hamiltonian [1], the best fit parameters are $|g| = 0.646$ and $A = 0.0605 \text{ cm}^{-1}$ for $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$ with g'_N set equal to 0.0. The resonance field for the sixth allowed transition (the highest resonance field) is 14,623 G, which is beyond our maximum obtainable magnetic field (13,500 G). Compared to the value of $|g|$ for $\text{Pr}^{4+}/\text{BaSnO}_3$, the value for $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$ is larger. This means that the crystal field strength in $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$ is weaker than that in $\text{Pr}^{4+}/\text{BaSnO}_3$ (see Fig. 5). Since the lattice parameter a for $\text{Ba}_2\text{Pr}_{0.02}\text{Sn}_{0.98}\text{O}_4$, and therefore the distance between Pr^{4+} and O^{2-} ($=a/2$), is larger than that for $\text{BaPr}_{0.02}\text{Sn}_{0.98}\text{O}_3$ (see Table 1), the crystal field strength around the

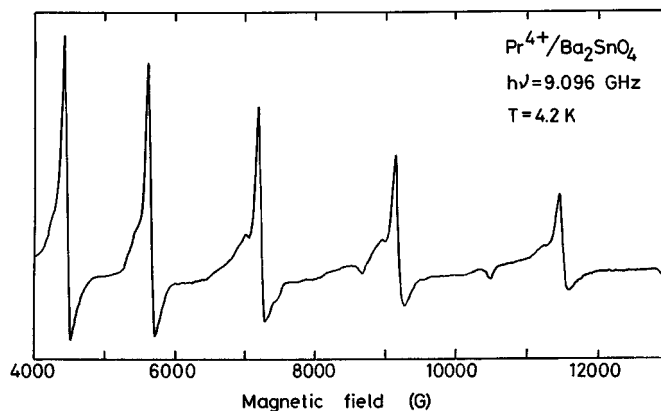


FIG. 6. EPR spectrum for Pr^{4+} ion doped in Ba_2SnO_4 measured at 4.2 K.

Pr^{4+} ions should be weaker in $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$ than that in $\text{Pr}^{4+}/\text{BaSnO}_3$. The present experimental result is in agreement with the crystallographic consideration that the value of $|g|$ increases with decreasing crystal field strength. On the other hand, the value of A is almost constant.

Figure 7 shows the EPR spectrum for Pr^{4+} doped in $\text{Ba}_3\text{Sn}_2\text{O}_7$ measured at 4.2 K. In this spectrum, five strong EPR absorption lines are observed with several weak absorption lines, some of which are not very weak in this case. Compared with Figs. 2 and 6, these weak EPR absorption lines are found to be attributable to the EPR absorptions for $\text{Pr}^{4+}/\text{BaSnO}_3$ and $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$ (see Fig. 7). These impurity specimens $\text{Pr}^{4+}/\text{BaSnO}_3$ and $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$ were probably formed in the cooling process of the preparation of $\text{Pr}^{4+}/\text{Ba}_3\text{Sn}_2\text{O}_7$. The fit of the experimental EPR absorption line positions to the calculated line positions was performed in the same way as for $\text{Pr}^{4+}/\text{BaSnO}_3$ and $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$. The $|g|$ value and hyperfine coupling constant A obtained are 0.606 and 0.0608 cm^{-1} , respectively. They are listed in Table 1. The hyperfine coupling constant for $\text{Pr}^{4+}/\text{Ba}_3\text{Sn}_2\text{O}_7$ is comparable to those for $\text{Pr}^{4+}/\text{BaSnO}_3$ and $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$. On the contrary, the g value is between that for $\text{Pr}^{4+}/\text{BaSnO}_3$ and that for $\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$.

Both Ba_2SnO_4 and $\text{Ba}_3\text{Sn}_2\text{O}_7$ are Ruddlesden-Popper-type phases, in which a second kind of stacking unit of the perovskite layer is involved (two-dimensional structure). On the other hand, BaSnO_3 has a simple perovskite structure

TABLE 1
Lattice Parameters and Spin-Hamiltonian Parameters

	Lattice parameters (Å)	$\text{Pr}^{4+}\text{-O}^{2-}$ (Å)	$ g $	A (cm^{-1})
$\text{Pr}^{4+}/\text{BaSnO}_3$	$a = 4.124$	2.062	0.583	0.0589
$\text{Pr}^{4+}/\text{Ba}_2\text{SnO}_4$	$a = 4.140, c = 13.295$	2.070	0.646	0.0605
$\text{Pr}^{4+}/\text{Ba}_3\text{Sn}_2\text{O}_7$	$a = 4.129, c = 21.460$	2.065	0.606	0.0608

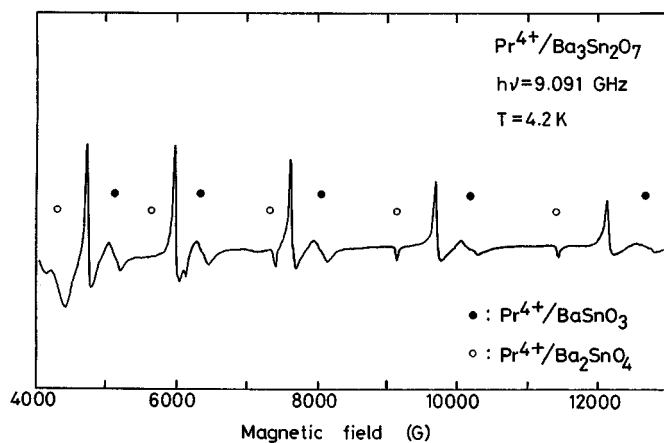


FIG. 7. EPR spectrum for Pr⁴⁺ ion doped in Ba₃Sn₂O₇ measured at 4.2 K.

and the octahedra formed by six oxygen ions are linked three-dimensionally (see Fig. 1). Their lattice parameters are listed in Table 1. In all of the host materials, Pr⁴⁺ ions are substituted for Sn⁴⁺ ions; therefore, the Pr⁴⁺ ions sit at the center of the oxygen octahedra and are influenced by the crystal field. The distances between Pr⁴⁺ and O²⁻ ions are half of the lattice parameter *a*. The Pr⁴⁺–O²⁻ distance is shortest for Pr⁴⁺/BaSnO₃ (2.062 Å) and longest for

Pr⁴⁺/Ba₂SnO₄ (2.070 Å), which means the crystal field is strongest in the former and weakest in the latter. The value of $|g|$ should decrease with increasing crystal field strength (see Fig. 5). We can conclude that the EPR results on $|g|$ are explained by considering the crystal field strength (Table 1) and that whether the host materials have a layered structure or not does not influence the $|g|$ value in this case.

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REFERENCES

1. J. B. Goodenough and J. M. Longo, in "Landolt-Börnstein Tabellen" (K.-H. Hellwege and A. M. Hellwege, Eds.), Neue Serie, III Band, 4a, Chap. 3. Springer-Verlag, Berlin, 1970.
2. Y. Hinatsu and N. Edelstein, *J. Solid State Chem.* **112**, 53 (1994).
3. A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Chap. 5. Oxford University Press, London, 1970.
4. N. F. Ramsey, "Molecular Beams." Clarendon Press, Oxford, 1956.
5. J. D. Axe, H. J. Stapleton, and C. D. Jeffries, *Phys. Rev.* **121**, 1630 (1961).
6. C. A. Hutchinson and B. Weinstock, *J. Phys. Chem.* **32**, 56 (1960).
7. B. R. Judd, "Operator Techniques in Atomic Spectroscopy." McGraw-Hill, New York, 1963.
8. Y. Hinatsu, T. Fujino, and N. Edelstein, *J. Solid State Chem.* **99**, 182 (1992).
9. Y. Hinatsu, *J. Alloys Compd.* **203**, 251 (1994).